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LITIGATED METAL CLUSTERS - STRUCTURES, ENERGY AND REACTIVITY

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Final Report

Air Force Research Laboratory
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14. ABSTRACT

Work has continued on two projects supported by AFOSR. We continued to improve the projection superposition approximation (PSA) algorithm through a more careful consideration of how to calculate cross sections for elongated molecules, especially if they are bent at sharp angles. The completed algorithm is now available for worldwide use on a dedicated server/website at UCSB. We have also continued to pursue the assembly of amino acids and small peptides, processes that are crucial both in materials science and in understanding the amyloid cascade process in biology. Finally significant work was done on the construction of a new instrument that will allow the study of size and shape selected metal and metal oxide clusters. These clusters are of central importance both fundamentally and in understanding heterogeneous catalysis at a molecular level.

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FINAL REPORT

When the original proposal was written it was hoped that funding of a new instrument through a DURIP grant would have been made and construction well along before the grant started (June 2011). The new instrument is designed to create clusters of a wide variety of species with emphasis on metal and metal oxides, both bare and ligated. These clusters could then be mass and shape selected and selectively reacted with a host of molecular reagents. Unfortunately that was not to be. Due to the macro economic conditions at the Federal level the DURUP grant was delayed two years. The repercussions of the economic downturn were even worse for the State of California and as a consequence University budgets were cut. In order to protect faculty appointments, staff appointments were either eliminated or put on hold. Hence once the DURIP funds finally arrived on campus the situation in the workshops (machine and electronics) at UCSB in general and in the Department of Chemistry in particular was uncertain leading to turmoil and inefficient performance. To complete this perfect storm, Dr. Paul Kemper, who had worked in the Bowers group his entire career, decided to retire. Paul is one of the premier instrument makers in the US and had designed the instrument ultimately funded by the DURIP grant. Paul's retirement meant extensive training needed to be done to get other group members up to speed in instrument construction and significantly slowed the construction of the new instrument. In addition it meant that personnel funds from this grant were needed to do this training and then the eventual construction itself.

Since the new instrument was not available we couldn't pursue the metal/metal oxide research initially intended and we had to focus on secondary objectives. There were two areas we chose for this purpose. The first was the development of a new algorithm for calculating collision cross sections on ionic species from model structures. Such algorithms are essential for molecular interpretation of experimental cross sections measured using ion mobility. There was urgent need for a fast and accurate algorithm that could be used over the entire size range of systems currently being investigated. Our new algorithm, the projection superposition approximation (PSA) is now complete. We have made it available free of charge to the scientific community on a dedicated website at UCSB. We also included a training protocol for all new prospective users. There now are over 50 users and the numbers are growing rapidly. The algorithm could not simply be distributed due to its complexity and size. The Bowers group, in cooperation with UCSB, provide the resources to support this website. It has applications across the chemical sciences from materials to biology.

The second research effort focused on the spontaneous assembly of systems into specific terminal structures. There is growing understanding of the importance of these processes but little understanding of the mechanisms at play. Our primary efforts were directed to the non-covalent assembly of amino acids and small peptides of importance to materials science, biochemistry/biology and medicine. For example, for the first time our work enabled an understanding of how water is essential in the assembly of di-phenylalanine, a promising new material. In a second example, the amino acid phenylalanine is known to cause the metabolic disease phenylketonuria (PKU) that attacks infants and young children who lack a particular regulating enzyme. However nothing was known about

the mechanism until our recent paper on phenylalanine assembly showing that at physiological concentrations characteristic of PKU it forms specific tube like structures with the hydrophobic phenyl groups OUTSIDE and the hydrophilic zwitterions INSIDE, the first such self assembled structures that spontaneously form in water of any type. These tube-like structures can then insert into the neuron membrane disrupting the ionic balance in the cell.

In all, ten papers were published with AFOSR support over the lifetime of the grant with five of these published since the last annual report (June 2014). The new publications are listed elsewhere in this report. Several of them were joint with other funding agencies but in all cases AFOSR support was essential for successful completion of the work.

1.

1. Report Type

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Principal Investigator Name

The full name of the principal investigator on the grant or contract.

Michael T. Bowers

Program Manager

The AFOSR Program Manager currently assigned to the award

Michael Berman

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Abstract

Work has continued on two projects supported by AFOSR. We continued to improve the projection superposition approximation (PSA) algorithm through a more careful consideration of how to calculate cross sections for elongated molecules, especially if they are bent at sharp angles. The completed algorithm is now available for worldwide use on a dedicated server/website at UCSB. We have also continued to pursue the assembly of amino acids and small peptides, processes that are crucial both in materials science and in understanding the amyloid cascade process in biology. Finally significant work was done on the construction of a new instrument that will allow the study of size and shape selected metal and metal oxide clusters. These clusters are of central importance both fundamentally and in understanding heterogeneous catalysis at a molecular level.

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Archival Publications (published) during reporting period:

1. Ion Mobility Spectrometry: A Personal View of its Development at UCSB
Bowers, M. T.
Int. J. Mass Spectrom. 2014, 370, 75-95.

2. Diphenylalanine Self Assembly: Novel Ion Mobility Methods Show the Essential Role of Water
Do, T. D.; Bowers, M. T.
Anal. Chem. 2015, 87, 4243–4252.

3. A New Algorithm to Characterise the Degree of Concaveness of a Molecular Surface Relevant in Ion Mobility Spectrometry
Wyttenbach, T.; Bleiholder, C; Anderson, S. E.; Bowers, M. T.
Mol. Phys. 2015, 15-16, 2344–2349.

4. Molecular Structures and Ion Mobility Cross Sections: Analysis of the Effects of He and N2 Buffer Gas
Bleiholder, C.; Johnson, N. R.; Contreras, S.; Wyttenbach, T.; Bowers, M. T.
Anal. Chem. 2015, 87, 7196–7203.

5. Amino Acid Metaclusters: Implications of Growth Trends on Peptide Self-Assembly and Structure
Do, T. D.; de Almeida, N. E. C.; LaPointe, N. E.; Chamas, A.; Feinstein, S. C.; Bowers, M. T.
Anal. Chem. 2016, 88, 868–876.

Changes in research objectives (if any):

The research objectives were changed from investigation of metal and metal oxide clusters to the self-assembly of various structures and to the development of a new algorithm for calculation of collision cross sections. The reasons for these changes are given in the final report.

Change in AFOSR Program Manager, if any:

Extensions granted or milestones slipped, if any:

AFOSR LRIR Number

LRIR Title

Reporting Period

Laboratory Task Manager

Program Officer

Research Objectives

Technical Summary

Funding Summary by Cost Category (by FY, $K)

	Starting FY	FY+1	FY+2
Salary			
Equipment/Facilities			
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Total			

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Appendix Documents

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